hour before all of the sodamide had reacted, and then 16 ml. (0.4 mole) of methanol (Baker C.P.) was added very rapidly. As soon as the deep red color of the 3-phenylcyclohexenyl anion had disappeared, 15 g. (0.28 mole) of ammonium chloride was added to neutralize the sodium methoxide that was formed.[8] Approximately 100 ml. of ether was added and the ammonia allowed to evaporate. The hydrocarbon products were recovered in the same manner as in the reactions of phenylallylsodium with methanol above and distilled in a Hickman vacuum still. A colorless distillate (n^{20}D 1.5603, λ_{max} 247 mμ, ϵ_{max} 8410) was recovered in 92% yield. Careful distillation through the twisted wire gauze column at 15 mm. pressure gave 33% 3-phenylcyclohexene and 67% 1-phenylcyclohexene.

The refractive index of the 1-phenylcyclohexene was 1.5692 as compared to the literature value[11] of n^{20}D 1.5670. Based on $d^{20}{}_4$ 0.9934[11] and n^{20}D 1.5692, the molar refraction for 1-phenylcyclohexene was found to be 52.17, calcd. 51.35. The exaltation was 0.82. The ultraviolet absorption showed only one maximum at 247 mμ (ϵ_{max} 12940) and the 283 and 292 mμ peaks normally found in compounds of the type $C_6H_5CH{=}CHR$ were absent. The principal infrared absorption bands are given in Table II.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.09; H, 8.94.

Based on ultraviolet absorption spectra, refractive indexes and fractional distillation, the amounts of 1-phenylcyclohexene present in the reaction products were 63, 64 and 67%, respectively, and 3-phenylcyclohexene, 37, 36 and 33%, respectively.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Persulfate-initiated Oxidation of Vinyl Monomers in Aqueous Solutions[1]

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The reaction of oxygen with vinyl monomers in aqueous solution in the presence of potassium persulfate has been studied in detail. Rates of oxygen absorption have been obtained for acrylonitrile, methyl vinyl ketone and methacrylonitrile, and rates of monomer disappearance for the first two. The experimental data support the proposal that the reaction is a simplified copolymerization, involving the direct attack of persulfate on the monomer as one of the initiation steps. A comparison of rates of oxygen absorption gives the order of reactivity of monomers toward the peroxy free radical, which is in line with *Q*-values for these monomers. A study of the oxidation products shows that the polymeric peroxide resulting from the copolymerization may not always survive the aqueous media, but the monomeric products may be explained as arising from the decomposition of the peroxide, followed by further oxidation of some primary products.

In an earlier paper[2] the effect of oxygen on the polymerization of acrylonitrile in aqueous solution was investigated by following the rates of absorption of oxygen and determining the products of the oxidation. The results gave evidence for the formation of a polymeric peroxide, which subsequently decomposed to give a variety of products of low molecular weight. A tentative mechanism was suggested, but it could not be rigorously correlated with experimental results because of the lack of information concerning the kinetics of acrylonitrile disappearance.

A suitable method of analysis for acrylonitrile has now been developed,[3] which has made possible more detailed study of the oxidation of acrylonitrile by simultaneous determination of the rates of absorption of oxygen and disappearance of monomer. It was also desired to extend the investigation of the oxidation products of acrylonitrile and to study other vinyl monomers, such as methyl vinyl ketone and methacrylonitrile.

Experimental and Results

Apparatus for Kinetic Experiments.—For the kinetic studies with acrylonitrile and methyl vinyl ketone the reaction flask was immersed in a water-bath at 50 ± 0.1° and was connected to constant pressure equipment of the type described by McBurney.[4] A minimum of connecting tubing was used, joints were of glass wherever possible, and water from the constant temperature bath was circulated through the jacket of the gas buret.

In the kinetic experiments with methacrylonitrile the pressure adjustment was manual, rather than automatic, and the gas buret was maintained at 50 ± 0.2° by means of an electrically-heated air jacket.

Polarographic Equipment.—The Heyrovsky polarograph, Sargent Co., model XII, was used for all analyses for acrylonitrile and methyl vinyl ketone. The dropping mercury electrode was of the Heyrovsky type. The drop time (t) in 0.02 M tetramethylammonium iodide was 5.11 sec. The mercury mass (m) was 1.0467 mg. per sec. The value of $m^{2/3}t^{1/6}$ was 1.35 mg.$^{2/3}$sec.$^{-1/2}$. The Sargent–Heyrovsky erlenmeyer type electrolysis vessel was placed in a circulating water-bath at 25.0 ± 0.1°. Mercury was purified to pass the foam test when shaken with distilled water.

Materials. Acrylonitrile.—Eastman Kodak Co. material was dried over calcium chloride, distilled through a 50-cm. Vigreux column, and stored over calcium chloride. Portions were redistilled immediately before use; n^{25}D 1.3886.

Methyl Vinyl Ketone.[5]—The 85% azeotrope with water was treated with anhydrous potassium carbonate and calcium chloride during cooling, followed by distillation at a pressure of 2 to 3 mm.; n^{22}D 1.400.

Methacrylonitrile.[6]—The inhibitor was removed by washing with 1% sodium hydroxide, water, drying over calcium chloride and redistilling. The fraction boiling at 90–90.3° was used at once.

Potassium Persulfate.—Baker and Adamson Reagent Grade was recrystallized from water at 50°. Iodometric analysis indicated a purity of better than 99.5%.

Other Materials.—Eastman Kodak Co. tetramethylammonium iodide was recrystallized twice from 50% aqueous ethanol. Methyl isopropenyl ketone dimer was depolymerized by heating at 200°, and the monomeric form was redistilled under reduced pressure immediately before use. Acrylamide[7] was used without recrystallization.

Procedures for Kinetic Experiments.—The following procedure was used for experiments with acrylonitrile and methyl vinyl ketone. With the reaction system and gas buret at 50°, an accurately weighed amount of potassium persulfate and 50 ml. of distilled water were added to the

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[1] From the Ph.D. Theses of Oscar A. Pickett, Jr., and Sterling F. Strause (1955) and the M.S. Theses of Sterling F. Strause (1953) and Howard E. Worrell, Jr. (1950). Supported in part by grants NSF-G193 and NSF-G578 from the National Science Foundation.

[2] K. C. Smeltz and E. Dyer, THIS JOURNAL, **74**, 623 (1952).

[3] S. F. Strause and E. Dyer, *Anal. Chem.*, **27**, 1906 (1955).

[4] L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1251 (1949).

[5] Kindly supplied by the Jackson Laboratory of E. I. du Pont de Nemours and Co., Inc.

[6] Kindly furnished by the Shell Development Company.

[7] Supplied through the courtesy of Dr. W. M. Thomas, American Cyanamid Co.

flask. After flushing the system with oxygen while stirring for 20 minutes, the monomer and an additional 50 ml. of water were added. Ten minutes was allowed for the system to reach equilibrium temperature and vapor pressure. The system was then adjusted to atmospheric pressure and set for constant pressure regulation. Measurements of oxygen absorption were made at hourly intervals, and 1.0-ml. samples were withdrawn for analysis at specified times. The oxygen absorption data were corrected for the volume of samples removed.

The newly-developed polarographic method of analysis,[3] which allows the determination of acrylonitrile in the presence of a known concentration of potassium ion, was used for the analysis of samples from acrylonitrile reaction mixtures. The solutions for analysis were 6.00 × 10^{-4} *M* with respect to hydroquinone and 0.02 *M* with respect to tetramethylammonium iodide. A polarographic[8,9] method was also used to determine methyl vinyl ketone. For these analyses 0.1 *M* potassium chloride served as the supporting electrolyte.

In the experiments with methacrylonitrile, the general procedure was essentially the same as with the other monomers. A total of 300 ml. of water was used, and 30 minutes were allowed for the reaction mixture to reach equilibrium temperature and vapor pressure after the addition of the monomer.

Kinetic Data. A. Acrylonitrile.—The dependence of the rates of absorption of oxygen and of disappearance of monomer on the initial concentrations of acrylonitrile and of potassium persulfate was determined by systematic variation of the concentration of each reactant while holding the other constant. Representative data are given in Table I. The units of moles hr.$^{-1}$ were chosen to express the initial rates in comparable terms. The linear initial slopes for oxygen absorption were determined over periods of 7 hours; for monomer disappearance, over periods of 12 hours. The method of least squares was used in obtaining the best values for all slopes, and probable errors were evaluated. Graphs of oxygen absorption data were similar to those reported earlier.[2] The data for acrylonitrile disappearance in three typical runs are summarized in Fig. 1, which illustrates the dispersion of the points about a straight line. Statistical analysis showed that the data for individual runs could best be represented by straight lines during the 12-hour period.

TABLE I

VARIATION OF INITIAL RATES[a] WITH CONCENTRATIONS OF MONOMER AND PERSULFATE

(Monomer),[b] *M* × 10	($K_2S_2O_8$),[b] *M* × 10^2	$-dO_2/dt$,[c] moles hr.$^{-1}$ × 10^4	$-d$(Monomer)/dt,[c] moles hr.$^{-1}$ × 10^4
	Acrylonitrile		
0.58 ± 0.01	7.2	1.03 ± 0.01	0.9 ± 0.1
2.55 ± 0.02	7.2	2.33 ± 0.04	3.2 ± 0.1
7.22 ± 0.05	7.2	4.5 ± 0.1	7.7 ± 0.4
1.26	1.83	....	0.49 ± 0.05
1.26	7.33	....	2.0 ± 0.1
7.5	1.75	1.73 ± 0.02	....
7.5	6.98	4.6 ± 0.1	....
7.5	6.98	4.5 ± 0.1	....
	Methyl vinyl ketone		
2.40	7.40	2.37	2.5
7.24	7.40	4.66	6.4
12.01	7.40	6.60	12.0
7.18	1.85	2.82	6.9
7.18	5.55	4.62	13.3
7.24	9.25	5.46	15.8

[a] Volume of reaction mixture was 100 ml. [b] Initial concentrations. [c] Typical data, a small fraction of that used to determine rate constants.

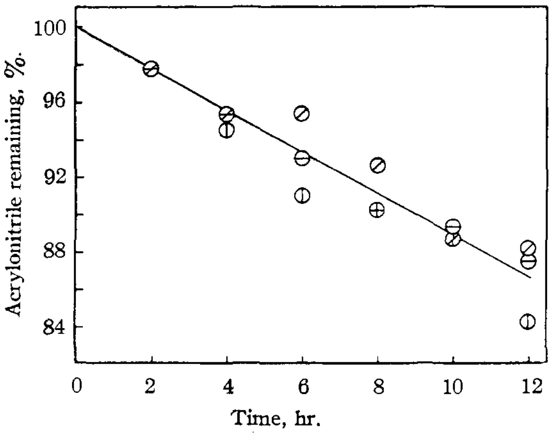

Fig. 1.—Initial slopes for acrylonitrile disappearance at constant initial concn. of $K_2S_2O_8$ of 0.072 *M*; init. concn. of acrylonitrile: ⦶, 0.255 *M*; ⊖, 0.541 *M*; ⦶, 0.722 *M*.

From the variation of initial slopes with concentration the orders of reaction were calculated for each series of runs. The arithmetic mean was derived from all possible combinations in a given series, and probable errors were evaluated. The over-all rate expressions were found

$$-d(\mathrm{ACN})/dt = k_a(\mathrm{ACN})^{0.80 \pm 0.11}(K_2S_2O_8)^{1.1 \pm 0.2} \quad (1)$$

$$-d(O_2)/dt = k_b(\mathrm{ACN})^{0.65 \pm 0.04}(K_2S_2O_8)^{0.69 \pm 0.04} \quad (2)$$

It may be noted that the expression for the absorption of oxygen does not agree with the one which was previously suggested.[2] However, the raw data obtained in the earlier investigation[10] do indeed agree with the current results, and when the original data are used to calculate the orders of reaction, the expression results

$$-d(O_2)/dt = k_b(\mathrm{ACN})^{0.62}(K_2S_2O_8)^{0.63} \quad (3)$$

As a means of determining the relative molar quantities of monomer and oxygen which were reacting, the ratios of d(ACN)/d(O_2), expressed in moles hr.$^{-1}$, were calculated. These ratios were found to vary from 1.0:1 to 1.7:1 and were dependent on the concentration of the reactants.

B. Methyl Vinyl Ketone.—Representative kinetic data are also given in Table I. The linear initial slopes for oxygen absorption were determined during 7 hours, while those for monomer disappearance were limited to 3 or 4 hours. The precision was of the same order of magnitude as for acrylonitrile. In general, the rate of reaction was faster than in the case of acrylonitrile. By calculating the orders of reaction from initial slopes, the following kinetic expressions were obtained.

$$-d(\mathrm{MVK})/dt = k_c(\mathrm{MVK})^{1.0 \pm 0.2}(K_2S_2O_8)^{0.5 \pm 0.1} \quad (4)$$

$$-d(O_2)/dt = k_d(\mathrm{MVK})^{0.7 \pm 0.1}(K_2S_2O_8)^{0.4 \pm 0.1} \quad (5)$$

The ratios of d(MVK)/d(O_2) were not so significant in this case. No regular dependence on monomer concentration was observed, and the variation with persulfate concentration was not well defined. The values ranged from 1.7:1 to 2.9:1 for these initial periods.

The rates of oxygen absorption by methyl vinyl ketone decreased steadily after 7 hours to become almost negligible after 40 hours, while the curves for monomer disappearance showed accelerated slopes. At the end of these reactions approximately six moles of methyl vinyl ketone had been consumed for every mole of oxygen. This indicates that monomer was consumed by some reaction other than that occurring in the initial period. Although polymerization to products of high molecular weight was completely inhibited during the experiments with methyl vinyl ketone, it is believed that dimer or trimer may have been formed. No definite evidence has been obtained in support of this hypothesis, but several lines of indirect evidence[11] seem to indicate this possibility.

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[8] E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem.. Anal. Ed.*, **16**, 469 (1944).

[9] C. W. Johnson, C. G. Overberger and W. J. Seagers, THIS JOURNAL, **75**, 1495 (1953).

[10] K. C. Smeltz, Ph.D. Thesis, University of Delaware, June, 1951.

[11] O. A. Pickett, Ph.D. Thesis, University of Delaware, June, 1955.

C. **Methacrylonitrile.**—Only oxygen absorption data were obtained for methacrylonitrile. The effect of variation of monomer concentration was not determined because of the limited solubility of methacrylonitrile in water. The rate of absorption of oxygen by 300 ml. of 0.333 *M* aqueous methacrylonitrile varied from 2.5×10^{-4} mole per hour at an initial persulfate concentration of 0.00309 *M* to 6.1×10^{-4} mole per hour at a persulfate concentration of 0.0185 *M*. In this range the initial rates varied with the 0.6 power of the persulfate concentration. At higher concentrations the rate was independent of the persulfate concentration. In the experiments with methacrylonitrile the oxygen did not inhibit the normal polymerization completely, even at low concentrations of persulfate.

D. **Other Monomers.**—Methyl isopropenyl ketone and acrylamide were investigated briefly, and it was found that solutions of these monomers absorbed oxygen in the same manner as the other monomers. Oxygen absorption by methyl isopropenyl ketone solutions was greater than in the case of methyl vinyl ketone, while acrylamide solutions absorbed oxygen at a slower rate than acrylonitrile. Polymerization to products of high molecular weight was completely inhibited by the presence of oxygen. Linear initial slopes over 7-hour periods, using an initial persulfate concentration of 0.0370 *M*, gave the following values of $-\mathrm{d}O_2/\mathrm{d}t$, in moles $\mathrm{hr.}^{-1} \times 10^4$: for 0.0353 *M* and 0.0362 *M* methyl isopropenyl ketone, 2.69 and 2.71, respectively, and for 0.095 *M* acrylamide. 2.81.

Oxidation Products of Acrylonitrile.—In order to obtain relatively large quantities of oxidation products under conditions which resembled the kinetic studies as closely as possible, reaction mixtures consisting of 10.0 g. of potassium persulfate and 30 ml. of acrylonitrile in 500 ml. of water were heated at 50–55°, while stirring and passing oxygen through the solution. Three runs were conducted for 49, 71 and 83 hours, respectively, and only the first of these showed polymer formation after the stirring was stopped at the end of the run. The reaction mixture, free of polymer, was fractionally distilled at a pressure of 15–20 mm. with a bath temperature not above 50°. The aqueous distillates were found to contain hydrogen cyanide, formaldehyde, formic acid and glycolic acid. The formic acid was isolated as the sodium or calcium salt, subsequently liberated and reduced to formaldehyde with acid and magnesium. The glycolic acid was isolated as calcium glycolate, which gave the characteristic chromotropic acid test on heating.[12] After the main portion of the reaction mixture had been distilled, the remaining mixture of 10–15 ml. of solution and inorganic salts was treated with excess ethanol to precipitate the major portion of the remaining salts, which consisted of potassium persulfate, and potassium and ammonium sulfate and bisulfate. The ethanolic filtrate was distilled under reduced pressure, resulting in a residual, sirupy liquid and a distillate containing small amounts of formaldehyde and hydrogen cyanide.

The sirupy liquid was found to consist almost entirely of glyceronitrile. By treatment in basic aqueous medium at 15° with benzoyl chloride, a precipitate was obtained and recrystallized from aqueous ethanol to yield white needles, m.p. 93–94°, which did not lower the melting point of an authentic sample of glyceronitrile dibenzoate. The benzoate esters of glycolonitrile and of the dicyanohydrin of glyoxal were absent. Small amounts of glycolic acid and ammonium bisulfate were also found in the sirupy liquid. Since this liquid constituted a major portion of the oxidation products, it was concluded that glyceronitrile was a major, primary oxidation product of acrylonitrile.

Oxidation Products of Methyl Vinyl Ketone.—Some of the reaction mixtures from the kinetic studies were examined, and carbon monoxide, carbon dioxide and formic acid were identified. Efforts to separate a complex, carbonyl-containing fraction through chromatography of the 2,4-dinitrophenylhydrazones were unsuccessful. No formaldehyde or pyruvaldehyde could be found.

Oxidation Products of Methacrylonitrile.—Kinetic runs which were to be examined for products were allowed to continue for several days under a constant supply of oxygen. Normal polymethacrylonitrile and polymeric peroxide were separated from the aqueous solution by adding sodium chloride and centrifuging. The polymeric mixture was dissolved in acetone, and the solution was added to excess methanol to precipitate the polymethacrylonitrile. Distillation of the solvents under reduced pressure yielded an oily material which had the properties of an impure sample of polymeric peroxide. It initiated the polymerization of acrylonitrile in bulk, exploded on heating, and contained at least 9.9% peroxidic oxygen.

When the aqueous solution from a reaction mixture was made basic and extracted continuously with ether, a cyanohydrin was obtained which boiled at 100° at 19 mm., and which gave the 2,4-dinitrophenylosazone of pyruvaldehyde, identified after recrystallization from nitrobenzene, by mixed melting point (292°, uncor.) with an authentic specimen. These properties characterize the cyanohydrin of hydroxyacetone. Acetic acid was identified by refluxing with *p*-toluidine to yield *p*-methylacetanilide, which did not lower the melting point of an authentic sample.

Other products obtained from the aqueous reaction mixture were hydrogen cyanide, formaldehyde and a small amount of hydroxyacetone and/or pyruvaldehyde.

Oxidation of Glycolaldehyde and Formaldehyde.—Glycolaldehyde was oxidized under the usual conditions of the kinetic runs, using a concentration of aldehyde which corresponded to 15% of the acrylonitrile concentration in a typical kinetic run. The 100 ml. of reaction mixture, which was 0.129 *M* in glycolaldehyde and 0.0740 *M* in potassium persulfate, absorbed 0.00159 mole of oxygen in 28 hours. At the end of this period, oxygen absorption was negligible, only 7% of the glycolaldehyde remained, and the oxidation products were carbon dioxide, formaldehyde and glycolic acid. Tests for glyoxylic, oxalic and formic acids were negative. When formaldehyde was subjected to similar conditions, oxygen was absorbed and the oxidation products were carbon monoxide, carbon dioxide and formic acid.

Preparation of Glyceronitrile Dibenzoate.—Glyceronitrile, b.p. 110° at 0.75 mm., was prepared in poor yield by the cyanohydrin synthesis from glycolaldehyde. Benzoylation in pyridine yielded the dibenzoate, which can be obtained directly in good yield by the following procedure. To a cyanohydrin reaction mixture containing 0.0113 mole of glycolaldehyde and 0.012 mole of potassium cyanide in 35 ml. of water at 15° was added 0.023 mole of benzoyl chloride over a period of one hour. The solution was stirred vigorously and sodium hydroxide solution was added when necessary to keep the mixture basic to phenolphthalein. The product, obtained in 68.4% yield, gave white, needle-like crystals, m.p. 94.5–95.0° after several recrystallizations from ethanol.

Anal. Calcd. for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.44; N, 4.74. Found: C, 69.00, 69.20; H, 4.70, 4.60; N, 4.47, 4.48, 4.38, 4.74.

Discussion

Products of the Reaction.—Products previously obtained[2] from acrylonitrile were carbon dioxide, carbon monoxide, hydrogen cyanide, formaldehyde, glycolic acid and a cyanohydrin which was a derivative of either glycolaldehyde or glyoxal. The current work confirmed the identity of all these products and the cyanohydrin was definitely identified as the cyanohydrin of glycolaldehyde. Glycolonitrile and the dicyanohydrin of glyoxal were not present in detectable quantities.

It appears that glyceronitrile, the cyanohydrin of glycolaldehyde, is a major product of the oxidation of acrylonitrile in the aqueous media, and it seems to be the missing link between the polymeric peroxide and the final oxidation products. Glyceronitrile would result from a reductive cleavage of the peroxide linkages of the polymeric peroxide of acrylonitrile.

$$[\text{—OCH}_2\text{CH(CN)O—}]_n \longrightarrow n\text{-HOCH}_2\text{CH(CN)OH} \rightleftarrows \text{HOCH}_2\text{CHO} + \text{HCN}$$

The cyanohydrin would be equilibrated with glycolaldehyde and hydrogen cyanide, although the

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[12] E. Eegriwe, *Z. anal. Chem.*, **89**, 1921 (1932); *C. A.*, **26**, 4769 (1932).

equilibrium concentration of glycolaldehyde would be very small in the acidic medium. Control experiments showed that this aldehyde is readily oxidized under the prevailing conditions, and the products are glycolic acid, formaldehyde, and carbon dioxide. Thus it is seen that the continuous oxidation of the glycolaldehyde resulting from the cyanohydrin equilibrium would account for the accumulation of hydrogen cyanide, formaldehyde, glycolic acid and carbon dioxide. No detectable amounts of free glycolaldehyde were found in reaction mixtures. The polymeric peroxide, which has not been isolated from the aqueous systems, probably does not attain a high molecular weight.

A complete discussion requires the consideration of an alternative course of decomposition. If the peroxide linkages were thermally dissociated in a homolytic cleavage, followed by cleavage of the adjacent carbon to carbon bonds, the resulting products would be formaldehyde and formyl cyanide. The latter compound would probably react with water in the same manner as acetyl cyanide does,[13] resulting in the formation of formic acid and hydrogen cyanide. While this mode of decomposition does not account for the major products which were isolated, it is possible that it may take place to a limited extent.

The products resulting from the oxidation of methacrylonitrile show very definitely that the reaction involves the initial formation of a polymeric peroxide, as some of the polymeric peroxide remained undecomposed in the aqueous medium. Thermal decomposition of this peroxide[14] leads to the formation of formaldehyde and pyruvonitrile, and the latter reacts[13] with water to form acetic acid and hydrogen cyanide. Reductive cleavage[14] results in the formation of the cyanohydrin of hydroxyacetone. Hydroxyacetone is readily oxidized to pyruvaldehyde. In the current investigation, the aqueous reaction mixtures contained formaldehyde, acetic acid, hydrogen cyanide, hydroxyacetone and/or pyruvaldehyde. Good evidence has been obtained for the presence of the cyanohydrin of hydroxyacetone. Thus, the products indicate that both types of peroxide decomposition occurred in this case. The thermal decomposition to formaldehyde and pyruvonitrile would be expected, since appreciable amounts of the peroxide accumulated in the aqueous reaction mixtures.

Mechanism of the Reaction.—Since the products resulting from the reaction of oxygen with vinyl monomers in aqueous solutions of potassium persulfate indicate that the corresponding polymeric peroxide is first formed, the initial reaction should exhibit copolymerization kinetics. Bovey and Kolthoff[15] treated oxygen as a comonomer in the emulsion polymerization of styrene in an oxygen atmosphere, but the mode of termination of free radicals was not known. The following mechanism is now presented for the copolymerization of vinyl monomers with oxygen in aqueous solutions initiated by persulfate

Initiation:

$$S_2O_8^{=} \xrightarrow{k_1} 2SO_4^{-}\cdot \qquad (6)$$

$$S_2O_8^{=} + M \xrightarrow{k_2} {}^{-}SO_4 - M\cdot + SO_4\cdot^{-} \qquad (7)$$

Propagation:

$$R_1\cdot + O_2 \xrightarrow{k_3} R_2\cdot \qquad (8)$$

$$R_2\cdot + M \xrightarrow{k_4} R_1\cdot \qquad (9)$$

Termination:

$$R_1\cdot + R_2\cdot \xrightarrow{k_5} \text{Products} \qquad (10)$$

M represents a vinyl monomer, $R_1\cdot$ is a radical ending in monomer, and $R_2\cdot$ is a peroxy radical. In this mechanism it is assumed that (a) addition of monomer to a radical ending in monomer does not occur, (b) oxygen does not react with a peroxy radical, (c) cross-termination prevails and (d) some initiating radicals are formed by the direct reaction of monomer and initiator.

By using the assumption of the steady state and the method of kinetic analysis suggested by Alfrey, Bohrer and Mark,[16] the following rate expressions are obtained

$$-d(M)/dt = k_2(P)(M) + \sqrt{k_4K(P)(M)}\,\sqrt{k_1 + k_2(M)} \qquad (11)$$

$$-d(O_2)/dt = \sqrt{k_4K(P)(M)}\,\sqrt{k_1 + k_2(M)} \qquad (12)$$

where $K = 2\,k_3(O_2)/k_5$ and P = persulfate.

These equations become useful when one considers the limiting dependence on monomer and persulfate concentrations resulting when the various constants become negligibly small. By testing all the possibilities in this way, the limits can be determined for the exponents in the simplified rate expressions 13 and 14, which are the type derived from actual experimental data.

$$-d(M)/dt = K'(P)^a\,(M)^b \qquad (13)$$

$$-d(O_2)/dt = K''(P)^c\,(M)^d \qquad (14)$$

The predicted possible ranges for the exponents in equations 13 and 14 are compared in Table II with the values obtained from the experimental data.

TABLE II

COMPARISON OF EXPONENTS IN RATE EXPRESSIONS

Exponent	Predicted value	Actual value ACN[a]	MVK[a]	MACN[a]
a	0.5 to 1.0	1.1 ± 0.2	0.5 ± 0.1	
b	.5 to 1.0	0.80 ± .11	1.0 ± .2	
c	.5	.69 ± .04	0.4 ± .1	0.6
d	.5 to 1.0	.65 ± .04	0.7 ± .1	

[a] Acrylonitrile, methyl vinyl ketone and methacrylonitrile.

Reasonable agreement is shown for all the exponents, and it appears that the mechanism may be generally applicable. Further substantiation of the mechanism is found in the data from the acrylonitrile studies. From equations 11 and 12 it is seen that the two rate expressions differ only by the term k_2(P) (M). Therefore in a series of experiments in which the persulfate concentration is held constant, the difference between the rate of disappearance of monomer and the rate of oxygen ab-

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(13) F. C. Whitmore, "Organic Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 365.

(14) S. F. Strause and E. Dyer, THIS JOURNAL, **78**, 136 (1956).

(15) F. A. Bovey and I. M. Kolthoff, *ibid.*, **69**, 2143 (1947).

(16) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952, p. 202.

sorption should be directly proportional to the monomer concentration. A graph of these data for acrylonitrile gives a good straight line.

The correlation of the mechanism with the observed kinetics requires that both equations 6 and 7 must be involved in the initiation step. Kolthoff, Meehan and Carr[17] found that the kinetics of persulfate decomposition during the polymerization of allyl acetate could be interpreted on the assumption that persulfate did not react directly with the monomer; allyl acetate did not affect the initial rate of disappearance of persulfate. However, in this Laboratory Heinaman[18] found that when normal polymerization was inhibited by oxygen, the first-order decomposition of 0.0185 *M* potassium persulfate at 50° was doubled in the presence of 0.94 *M* acrylonitrile. In the current investigation it was found that methyl vinyl ketone also accelerated the decomposition under the usual reaction conditions. It is significant that first-order kinetics were retained in these decomposition experiments, for the proposed mechanism predicts that the decomposition of persulfate would show apparent first-order kinetics in the presence of a large excess of monomer. It is concluded that the system under investigation differs from the polymerization of allyl acetate in the mechanism of initiation.

While it is believed that the proposed mechanism operates practically exclusively in the reaction with acrylonitrile and is approximately closely in the case of methyl vinyl ketone in the early stages, the addition of the following steps has also been considered.

Propagation:

$$R_1\cdot + M \xrightarrow{k_6} R_1\cdot \qquad (15)$$

Termination:

$$R_1\cdot + R_1\cdot \xrightarrow{k_7} \text{products} \qquad (16)$$

The resulting rate expressions are more complex than the previous ones and the range of variation of the exponents *a*, *b* and *d* in equations 13 and 14 is extended, while *c* remains fixed at 0.5. Experimental facts indicate that these steps may occur to some extent with methyl vinyl ketone during the initial period.

Correlation of Reactivity with Structure.—Since it seems likely that the mechanism of reaction in the system under investigation is rather generally true for water-soluble vinyl monomers, a comparison of rates of reaction under identical conditions should lead to a correlation of reactivity with structure. Oxygen absorption data have been obtained for six monomers in this Laboratory. This rate seems to be less dependent on slight changes in mechanism than is the rate of monomer disappearance. It seems that changes in the structure of the monomer should be reflected extensively in the rate constant k_4, since this involves the addition of monomer to the peroxy free radical. Equation 12 shows that the rate of oxygen absorption varies with the square root of k_4. Thus, a monomer which is less reactive toward the peroxy free radical would show a smaller rate of oxygen absorption.

Data are not available for comparison of all the monomers under identical conditions, but values available allow the following assignment of orders of decreasing oxygen absorption rates: methyl vinyl ketone > acrylonitrile > acrylamide; methyl isopropenyl ketone > methyl vinyl ketone; acrylonitrile > acrylamide > methyl acrylate[18]; methacrylonitrile > acrylonitrile. Extrapolation of existing data indicates that methacrylonitrile is more reactive than methyl isopropenyl ketone and methyl vinyl ketone. On the basis of these comparisons the monomers may be listed in the following over-all order of decreasing rate of oxygen absorption: methacrylonitrile, methyl isopropenyl ketone, methyl vinyl ketone, acrylonitrile, acrylamide, methyl acrylate. It is proposed that this is the decreasing order of reactivity toward the peroxy free radical.

The average *Q*- and *e*-values[19] of four of these monomers are as follows: methacrylonitrile 1.07 and 0.9, methyl vinyl ketone 1.0 and 0.7, acrylonitrile 0.60 and 1.2, methyl acrylate 0.42 and 0.6, respectively. Excellent correlation with the *Q*-values is evident, while there is no apparent correlation with the *e*-values. The *Q*-value is a function of resonance stabilization and the *e*-value is a function of the polarity of the double bond. Therefore, it appears that resonance stabilization of the resulting free radical is more important than polarity of the double bond in determining the reactivity of a particular monomer toward the peroxy free radical.

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